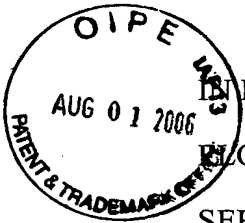


DOCKET NO: 220760US0PCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE



ENTIRE APPLICATION OF

ELORENCE L'ALLORET

SERIAL NO: 10/069,981

FILED: MARCH 14, 2002

FOR: DISPERSIONS STABILIZED AT
TEMPERATURES OF FROM 4 TO 50
DEGREES CELSIUS BY MEANS OF A
POLYMER COMPRISING WATER-
SOLUBLE UNITS AND UNITS WITH AN
LCST

:

: EXAMINER: EGWIM

:

: GROUP ART UNIT: 1713

:

APPEAL BRIEF

COMMISSIONER FOR PATENTS
ALEXANDRIA, VIRGINIA 22313

SIR:

This brief is submitted in response to the rejections dated April 5, 2006.

REAL PARTY OF INTEREST

The real party of interest herein is L'Oréal of Paris, France.

~~08/03/2006 JADD01 00000001 10069981~~
~~02 FC:1402~~ 500.00 OP

08/03/2006 JADD01 00000001 10069981
02 FC:1402 500.00 OP

RELATED APPEALS AND INTERFERENCES

An Appeal has been or will be filed in related application serial no. 10/069,983. This related application is being examined by the same Examiner and contains similar rejections as those outlined below.

STATUS OF CLAIMS

Claims 25-69 are active in this application.

Claims 27, 31, 34, 35, 37, 38, 46-48, 50-53, 56-60, and 62 were withdrawn from consideration by the Examiner.

Claims 25, 26, 28-30, 32, 33, 36, 39-45, 49, 54, 55, 61, and 63-69 are rejected.

STATUS OF AMENDMENTS

There are no outstanding amendments in this case.

SUMMARY OF CLAIMED SUBJECT MATTER

The claimed invention is directed to a dispersion comprising

- (1) at least one aqueous phase which contains a polymer and at least one oily phase;
- (2) the polymer comprising
 - a. water-soluble units and
 - b. units with an LCST, the units with an LCST having in water a demixing temperature of from 5 to 40°C at a concentration of 1% by mass,
 - c. the polymer formed of an oligomer or copolymer of water-soluble units wherein the polymer is water-soluble in a range of 5 to 80°C at a concentration of at least 10 g/l; and

- d. the polymer being present in the aqueous phase at a concentration such that the gel point of the aqueous phase is from 5 to 40°C, to ensure the stability of the dispersion when it is subjected to temperature variations in the range from 4 to 50°C

Why is this important and why does it distinguish over the cited prior art references?

As discussed in the specification on page 2, line 6- page 2, line 22, stability of cosmetic dispersions is very important because such dispersions are often stored and transported in a variety of temperatures sometimes at room temperature, sometimes at 4°C. Under these varied conditions the dispersion can demix (become heterogeneous) due to the loss in viscosity of the aqueous phase and would render the product unsatisfactory for consumer sale and use. This resultant heterogeneity of the dispersion is reflected by a phenomenon of sedimentation when the dispersed phase has a density greater than that of the continuous aqueous phase; this is the case for many aqueous suspensions of mineral particles. When the dispersed phase is less dense than the continuous aqueous phase, a phenomenon of creaming takes place, such as, for example, in the case of emulsions.

Further, as described in the specification on page 4, line 25 to page 5, line 31, the polymers include units with an LCST, which have, in water, a lower critical solution temperature. These LCST units have a modified solubility in water beyond a certain temperature. They are units having a heat-induced demixing temperature (or cloud point) defining their region of water solubility. The minimum demixing temperature obtained as a function of the polymer concentration is known as the "LCST" (Lower Critical Solution Temperature). For each polymer concentration, a heat-induced demixing temperature is observed; it is higher than the LCST, which is the minimum point of the curve. Below this temperature, the polymer is water-soluble, and above this temperature, the polymer loses its

water solubility. Thus, the polymers containing the LCST units in the manner as claimed have water-gelling properties as a result of temperature changes.

According to the invention, a polymer is selected whose units with an LCST have a demixing temperature of from 5 to 40 °C at a concentration of 1% by mass, so as to obtain the gelation of an aqueous phase containing this polymer in the desired range. Furthermore, the polymer concentration used is sufficient to allow interactions between units with an LCST borne by different macromolecules, and to obtain this gelation of the aqueous phase, thus making it possible to ensure the stability of the dispersion.

In fact, the specification also presented data demonstrating the advantageous effects of selecting the types of polymers claimed as opposed to other polymers.

Example 1 (page 32, line 20 through page 34, line 14) prepared an oil-in-water emulsion containing a polymer identified as “polymer 2.” Polymer 2 is described in Table 1 on page 27 and is composed of (1) a water-soluble backbone containing polyacrylic acid; and (2) LCST units as grafts—poly-N-isopropyl-acrylamide in a proportion of 49% based on the final weight of the polymer; achieving a 0.9% degree of grafting (mol %). The emulsion prepared in Example 1 was subjected to temperature changes over the range of 4 to 45°C and the macroscopic appearance and thus the stability of the composition was monitored. As concluded in the specification, the polymer improves the stability of the emulsion at 45°C while maintaining a low viscosity at 20°C.

As a comparison, the specification described another oil-in-water emulsion containing another polymer (crosslinked poly(2-acrylamido-2-methylpropane sulphonic acid), see Comparative Example on page 34, line 16 through page 36, line 5. Similar analyses were performed for this composition. As concluded in the specification, while the viscosity and stability of the comparative emulsion had similar properties at 4°C, the emulsion destabilized

at higher temperatures (45°C) where the composition containing polymer 2 did not destabilize.

ISSUES TO BE REVIEWED ON APPEAL

- (1) The first issue to be reviewed on appeal is the rejection of Claims 25, 26, 28, 30, 32, 33, 40-45, 49, 55 and 65-67 as being anticipated by U.S. patent no. 4,767,265 (“Merchant”)
- (2) The second issue to be reviewed on appeal is the rejection of Claims 25, 26, 28, 29, 33, 40-45, 49, 55 and 65-67 as being anticipated by U.S. patent no. 4,274,977 (“Koerner”).
- (3) The third issue to be reviewed on appeal is the rejection of Claims 25, 26, 28, 29, 32, 33, 39-45, 55 and 63-67 as being anticipated by U.S. patent no. 4,559,226 (“Fogel”).
- (4) The fourth issue to be reviewed on appeal is the rejection of Claims 25, 26, 28-30, 32, 33, 36, 39-45, 49, 54, 55, 61, 63, 64, and 65-69 as being anticipated by or obvious in view of EP 583814 or EP629649 (“the Maroy publications”)
- (5) The fifth issue to be reviewed on appeal is the rejection of Claim 49 under 35 U.S.C. § 112, second paragraph.

There remains an obviousness-type double patenting rejection in view of co-pending application serial no. 10/069,983. However, as this case is still pending, review of this rejection is not requested at this time.

ARGUMENTS

Summary of the Argument

There are fundamental differences between the claimed dispersion and specifically, the polymer defined in the claims, and the compositions and polymers described in the cited prior art references. Specifically, unlike the polymer defined in the claims, the polymers described in the cited prior art exhibited a cloud point (in other words, the polymers of the prior art are NOT water-soluble in a range of 5 to 80°C at a concentration of at least 10 g/l). The art relied upon by the Examiner in the rejections does not describe polymers as the ones selected in the claims, does not lead one to select such polymers, and, in fact, the Examiner has simply failed to provide factual basis to support the rejections.

It is well-settled law that the standard set forth in § 102(b) is that of novelty. Lack of novelty, i.e., anticipation requires strict identity between the claimed invention and that disclosed in the prior art reference. To anticipate a claim, a single prior art source must contain all of the essential limitations of the claim *Verdegaal Bros. v. Union Oil Co. of California* 2 USPQ2d 1051, 1053 (Fed. Cir. 1987). Put very simply, the claims specifically require that the polymer is water-soluble in a range of 5 to 80°C at a concentration of at least 10 g/l, which as one knows means that within the temperature range cited in the claims, the polymer does not exhibit a cloud point or LCST. This fact, which the Examiner has seemingly failed to appreciate, differentiates the claimed invention from the descriptions provided in the prior art.

Therefore, upon review of the facts of this case, it should be apparent that the claimed invention is not described by the cited art with sufficient specificity as to constitute anticipation or obviousness under U.S. patent law and therefore the rejections should be REVERSED.

Issue #1

Merchant's goal is to provide "novel demulsifier formulations and processes for dewatering and/or desalting conventional whole heavy petroleum crudes, heavy petroleum crude fractions, residue, fuel oils and refinery hydrocarbon fractions." (col. 3, lines 14-21) This is an entirely different field and purpose when compared to the invention and the problems it solves (maintaining stability and viscosity of a dispersion over a wide-range of temperatures). Therefore, the general descriptions provided in the Merchant patent simply would not lead one to select the types of polymers claimed. Moreover, Merchant does not describe, with any specificity, the polymer contained in the claimed dispersion. In fact, assessment of the polymers Merchant would lead one to different polymers.

The polymers disclosed in Merchant do not contain an oligomer or copolymer of water-soluble units as claimed (see the maleic anhydride grafted to an alkyl phenol formaldehyde resin in col. 6, lines 41-49), and the polymers disclosed in Merchant do not contain LCST units, which are one of the limitations that defines the claims over this reference—see the preferred p-nonyl phenyl formaldehyde resin having 10 moles of ethylene oxide in the Examples of Merchant (see col. 10, lines 42-45 and col. 11, lines 29-30).

This formaldehyde resin with 10 moles of ethylene oxide contained in the polymers are not LCST units as has been clearly shown in the Malcom and Rowlinson publication, now of record. What becomes clear from this publication is that the Merchant polymers described are those that have no LCST. In this Malcolm publication, Figure 6 (Page 926) shows the phase diagrams for polyethylene oxide (indicated in squares and crosses) in which above the curve there exists two phases, below the curve there exists one phase, and the lowest point of the curve defines the LCST. Therefore, this Figure shows that as the molecular weight of the polyethylene oxide gets smaller, the two phase domain also gets smaller. Also illustrated is that for a POE of 3000, the two phase domain is indicated as the oval in the Figure. Taken

together then, 10 units of polyethylene oxide as is the case in Merchant would only exhibit 1 phase, i.e., no LCST.

In maintaining this rejection, the Office states that the teachings of the reference are not as limited to the examples illustrated in the above-discussion because Merchant describes other demulsifiers in col. 5, including oxyalkylated amines, glycol resin esters, oxyalkylated polyols and oxyalkylated alkyl-phenol formaldehyde resins. The point is missed. The point here is that while the Merchant polymers may be water-soluble (col. 5, line 34), they do not contain LCST units as defined in the claims of this application, as shown by the uncontested evidence, of record and discussed above. Further, the species specifically exemplified by Merchant are exemplary of Merchant's emulsifiers and are simply not the same polymers as defined in the claimed method and that absent such a description, Merchant does not provide the requisite disclosure to select monomers of water-soluble and LCST units and arrange them in the manner that would be the same as the polymer defined in the claimed dispersion. This becomes even more apparent when recognizing that the teachings of Merchant would lead one to select polymers optimized for the dewatering and/or desalting of hydrocarbon oil as opposed to maintaining stability and viscosity of, for example, a cosmetic dispersion.

Using the language from MPEP §2131.02, one of ordinary skill in the art would not be able to "at once envisage" the polymers set forth in the claimed dispersion. In view of this, the claims cannot be anticipated by the Merchant disclosure.

Moreover, Merchant does not describe the arrangement set forth in dependent Claim 29, in which the polymer is either

- (1) water-soluble units alternating with units with an LCST; or
- (2) a graft polymer whose backbone is formed from water-soluble units and bears LCST grafts.

In fact, the Office has failed to provide any reasons why this claim has been rejected in view of Merchant.

Moreover, Merchant does not describe or provide any suggestion for providing the arrangement in Claim 32, wherein water-soluble units have a molar mass ranging from 1000 g/mol to 5 000 000 g/mol when they constitute the water-soluble backbone of a grafted polymer, or a molar mass ranging from 500 g/mol to 100 000 g/mol when they constitute a block of a multiblock polymer or when they constitute the grafts of a grafted polymer. In fact, the Office has failed to provide any reasons why this claim has been rejected in view of Merchant.

Moreover, Merchant does not describe or provide any suggestion for providing the arrangement in Claim 40, in which the demixing temperature of the units with an LCST is from 10 to 35°C, for a concentration in water of 1% by mass of the units with an LCST. In fact, the Office has failed to provide any reasons why this claim has been rejected in view of Merchant.

Moreover, Merchant does not describe or provide any suggestion for providing the arrangement in Claim 45, which is in the form of a cosmetic make-up or care composition. In fact, the Office has failed to provide any reasons why this claim has been rejected in view of Merchant. Moreover, this is apparent from the fact that Merchants compositions are in a form for dewatering and/or desalting of hydrocarbon oil.

Reversal of the rejection in view of Merchant is requested.

Issue #2

Koerner describes an alkyl polyether at the top of col. 8, which polymer has a cloud point, i.e., the polymer exhibits an LCST, at a specific temperature and concentration (col. 8, lines 1-6). This polymer, however, is different from the polymer defined in the claimed dispersion where the polymer does not exhibit an LCST. As discussed on page 5, lines 16-31 of the present application, the polymer as a whole does not exhibit an LCST and permits the formulation of transparent compositions while the LCST units facilitate gelation and stability of the dispersion. This is apparent from the limitations provided in Claim 25: “wherein the polymer is water-soluble in a range of 5 to 80°C at a concentration of at least 10 g/l.”

Moreover, the polymers described elsewhere in Koerner, e.g., columns 5 and 6, also have a cloud point (see col. 6, lines 24-29) and thus are not the same as the polymer defined in the claimed dispersion.

The rejection based on Koerner was maintained, at least in part, because “the particular polymer of example 8 has a cloud point at a higher concentration than the concentration recited in the claims.” (Page 5 of the Official Action of April 5, 2006) However, the polymers used in the claimed dispersions do not have a cloud point at a concentration of at least 10g/l or LCST unlike those in Koerner. The Office further supports the rejection because the abstract of Koerner states that the emulsifier is water-soluble. Certainly the Abstract states this, but a polymer can be water-soluble at a certain concentration and temperature and still have a cloud point within another temperature (see col. 6, lines 24-28 of Koerner “which may be dissolved in water in any ratio and which had a cloud point . . .”). Again, what is missing from Koerner is a description of polymers that meets the claimed limitation of water-solubility in a range of 5 to 80°C at a concentration of at least 10 g/l.

Withdrawal of the rejection in view of Koerner is requested.

Issue # 3

Fogel in col. 2 describes an alkoylester of a specific formula where R_2 can be either (a) or (b) and x is from 1 to 10 (see lines 53-62). Polyoxypropylene groups, e.g., when x is 10, have a molecular weight of 580 g/mol and as shown on the attached technical sheet have a demixing temperature, i.e., cloud point, at a 1% concentration of 65°C (see P600E) (Dow Corning Technical Sheet: polypropylene glycol). Furthermore, where x is less than 10, the demixing temperature, i.e., cloud point, is much greater than 65°C (see, e.g., P400E). Thus, it is quite clear that the polymers of Fogel have a cloud point, which clearly makes those polymers different from the polymers used in the claimed dispersion.

In maintaining this rejection previously (Office Action of July 15, 2005), the Office states: “applicant appears to be ignoring the polyoxyethylene portions of the water-soluble polymers, i.e., wherein y is from 1 to 20.” Applicants did not ignore this disclosure in Fogel and moreover, is not particularly relevant to the claimed invention. These polyoxyethylene portions are the water-soluble portion of the alkoylester esters. Said another way, the $-(OCH_2CH_2)_y$ is the water-soluble portion and $(R_2)_x$ is the LCST portion of the alkoylester ester.

Specifically, it has already been explained that alkoylester of a specific formula where R_2 can be either (a) or (b) and x is from 1 to 10 (see col. 2, lines 53-62) are those having cloud points within the range that the claimed polymers are to be water-soluble. The technical basis for this distinction is reiterated below.

Polyoxypropylene groups, e.g., when x is 10, have a molecular weight of 580 g/mol and have a demixing temperature, i.e., cloud point, at a 1% concentration of 65°C (see P600E) (Dow Corning Technical Sheet: polypropylene glycol—of record). Furthermore, where x is less than 10, the demixing temperature, i.e., cloud point, is much greater than 65°C (see, e.g., P400E). Therefore, the polymers in Fogel are unquestionably different from the polymer defined in the claims.

More recently, in the Office Action of April 5, 2006, the Office cites Fogel at col. 4, lines 46-50 concluding that “they would be water-soluble in the range claimed by applicant.” (page 5 of the Office Action). This portion of Fogel merely says such would be preferable but by no means provides suitable evidence to contradict the evidence and explanation that Applicants have provided which shows, quite clearly, that the polymers in Fogel simply are not the same as those claimed.

Moreover, as cited by the Office on page 5 of the April 5, 2006 Action, the cloud point of the alkoylate esters is preferably below 0°C. How is this a teaching for polymer being water-soluble in the range of 5 to 80°C as claimed?

Even more compelling is the fact that unlike the present claims which include a polymer, the alkxylate esters of Fogel are small molecules with low molecular weights are simply are not polymers (see also the compounds in col. 8, lines 40-45, col. 9, lines 33-42, col. 10, lines 14-24, col. 11, lines 1-7, col. 11, lines 51-60, col. 12, lines 40-49, col. 13, lines 23-30 and col. 14, lines 9-19 of Fogel)

Reversal of the rejection in view of Fogel is requested.

Issue #4

The Maroy publications are acknowledged on page 4, lines 23 of the present specification. The Maroy publications describe a polymer with water-soluble groups and LCST groups (page 2, lines 26-30 of EP '814). Maroy also describes that the groups with LCST can be copolymerized with the water-soluble groups or grafted onto a hydrosoluble skeleton (page 2, lines 34-44 of EP '814).

Maroy does not describe a polymer containing LCST units having a demixing temperature of 5 to 40°C at 1% by mass in water in the claimed method. In fact, the LCST units described in the Maroy publications do NOT have, in water, a demixing temperature of from 5 to 40°C at 1% by mass in water. Specifically, on page 2, lines 53-56 and page 3, lines 2-3 of EP '814 and col. 2, line 54 to col. 3, line 4, Maroy describes that the LCST units selected from polyethyleneglycol (POE), polyoxypropylene (POP) or polyoxide of ethylene and propylene (POEP). Furthermore, Examples 1.1, 1.2, 1.3, and 1.4 of EP '814 (Maroy) on pages 3-4, all describe polymers with POE5 as the LCST units, which is polyethyleneglycol with a molecular weight of 5000 g/mol. However, these polymers have a demixing temperature above 100°C at a concentration of 1 % by mass (see page 5, line 41, page 6, lines 37-39, and page 6, lines 57-59 of EP '814). Therefore, these polymers cannot be the same as the polymer defined in the claimed dispersion (having a demixing temperature of 5 to 40°C at 1% by mass in water).

In Example 2.3 (page 7) of EP '814 (Maroy), the polymer contains POP of a molecular weight of 600 as the LCST unit. However, unlike the polymer in the claimed dispersion, this polymer of Maroy has a demixing temperature of 48°C at a concentration of 1 % by mass. In Example 2.5 (pages 7-8) of EP '814 (Maroy), the polymer contains a POEP polymer with a molecular weight of approximately 1100. However, unlike the polymer in the

claimed dispersion, this polymer has a demixing temperature above 60°C (see Figure 3 of EP '814).

In the Examples of EP '649, Maroy describes the same example as 1.2 from EP '814 (see the reference to French application 9210224, which is the priority application of EP '814 in col. 6, line 40 and lines 54-56) and Examples 4 and 5 which include POE with a molecular weight of about 5000. For the same reasons as discussed above concerning EP '814, these specifically described polymers have a demixing temperature above 60°C and are therefore NOT the same as the polymer set forth in the claimed dispersion.

Having provided evidence that the polymers described by the Maroy publications do not necessarily, each and every time, have the properties of the polymer defined in the claimed dispersion, the rejections based on Maroy '814 and '649 should be withdrawn.

In maintaining this rejection, the Office takes the position that "the prior art teachings are not limited to the species of the examples. The LCST groups, as identified in applicant's specification, are generically taught by Maroy." Whether, generically, various monomers are described that could be combined is not the correct standard for anticipation. The prior art must disclose with sufficient specificity the claimed invention in a manner that would allow one of ordinary skill in the art to "at once envisage" the polymers set forth in the claimed dispersion. The Maroy publications do not do that. As discussed above in great detail, in fact, if one followed the direction that the Maroy publications provides, it would lead to polymers having different properties than the ones defined in the claims.

As for the alternative obviousness rejection raised in view of these two publication, there must be some suggestion in the prior art to achieve the claimed invention (as opposed to using the claims as a guide to reconstruct the prior art, as the Office has done here). There is simply nothing in Maroy which would lead one to select the polymers in the claims nor that in so selecting one would be able to maintain viscosity and stability of a dispersion over a

wide temperature range. This is even more apparent when considering the entirety of the Maroy teachings (as is required). While the '649 Maroy publication makes passing mention to cosmetics, it is abundantly clear that both of the publications are directed to designing polymers particular useful in the oil industry (see EP '814 at page 2, lines 8-11 and EP '649, page 2, col. 1, lines 21-29).

Reversal of the rejections in view of the Maroy publications is requested.

Issue #5

Claim 49 is rejected because “it is unclear if applicant is claiming a block polymer or graft polymer.” (Page 2 of the Official Action of April 5, 2006).

The essential inquiry pertaining to the requirement under 35 U.S.C. § 112, second paragraph is whether the claims set out and circumscribe a particular subject matter with a reasonable degree of clarity and particularity. Definiteness of claim language must be analyzed, not in a vacuum, but in light of:

- (A) The content of the particular application disclosure;
- (B) The teachings of the prior art; and
- (C) The claim interpretation that would be given by one possessing the ordinary level of skill in the pertinent art at the time the invention was made. See MPEP § 2173.02

The relevant section of Claim 49 as found in Appendix I is reproduced below for immediate reference:

wherein the polymer is in the form of a block polymer in the form of *a grafted* polymer whose backbone is formed from water-soluble units and *bears grafts consisting of units with an LCST* and which is partially crosslinked.

As explained previously, and as apparent from the plain language of Claim 49, the polymer is a block polymer with water-soluble units in the backbone having *grafts of LCST units*. How could this be any clearer? Applicants submit that one in this field having familiarity with the knowledge in the filed and the conventional terminology used to describe polymers, would understand what this claim means.

Reversal of the rejection under 35 USC 112, second paragraph is requested.

CONCLUSION

In view of the above remarks, Appellants request that all of the rejections be
REVERSED.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,
MAIER & NEUSTADT, P.C.
Norman F. Oblon



Daniel J. Pereira, Ph.D.
Registration No. 45,518

Customer Number

22850

Tel: (703) 413-3000
Fax: (703) 413 -2220
(OSMMN 06/04)



APPENDIX 1 (CLAIMS)

Claims 1-24 (Cancelled)

25. (Previously Presented) A dispersion comprising at least one aqueous phase and at least one oily phase, wherein the aqueous phase comprises a polymer comprising water-soluble units and units with an LCST, the units with an LCST having in water a demixing temperature of from 5 to 40°C at a concentration of 1% by mass, and the polymer being present in the aqueous phase at a concentration such that the gel point of the aqueous phase is from 5 to 40°C, to ensure the stability of the dispersion when it is subjected to temperature variations in the range from 4 to 50°C, wherein the polymer comprises an oligomer or copolymer of water-soluble units wherein the polymer is water-soluble in a range of 5 to 80°C at a concentration of at least 10 g/l.

26. (Previously Presented) The dispersion as claimed in claim 25, formed by an oil-in-water emulsion in which water is the aqueous phase.

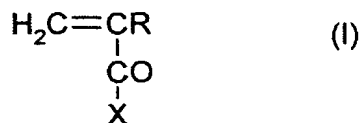
27. (Withdrawn) The dispersion as claimed in claim 25, formed by a water-in-oil-in-water multiple emulsion.

28. (Previously Presented) The dispersion as claimed in claim 25, formed by a dispersion of mineral and/or organic particles in the aqueous phase of an oil-in-water emulsion.

29. (Previously Presented) The dispersion as claimed in claim 25, in which the polymer is in the form of a block polymer comprising water-soluble units alternating with units with an LCST, or in the form of a grafted polymer whose backbone is formed from water-soluble units and bears grafts consisting of units with an LCST.

30. (Previously Presented) The dispersion as claimed in claim 25, in which the water-soluble units are obtained by free-radical polymerization of at least one monomer selected from the group consisting of :

- (meth)acrylic acid;
- vinyl monomers of formula (I) below:



in which:

- R is H, -CH₃, -C₂H₅ or -C₃H₇, and
- X is:
- alkyl oxides of -OR' type in which R' is a linear or branched, saturated or unsaturated hydrocarbon radical containing from 1 to 6 carbon atoms, optionally substituted with at least one halogen atom selected from the group consisting of iodine, bromine, chlorine and fluorine; a sulfonic (-SO₃⁻), sulfate (-SO₄⁻), phosphate (-PO₄H₂); hydroxyl (-OH); primary amine (-NH₂); secondary amine (-NHR₁), tertiary amine (-NR₁R₂) or quaternary amine (-N⁺R₁R₂R₃) group with R₁, R₂ and R₃ being, independently of each other, a linear or branched, saturated or unsaturated hydrocarbon radical containing 1 to 6 carbon atoms, with the proviso that the sum of the carbon atoms of R' + R₁ + R₂ + R₃ does not exceed 7; and
- -NH₂, -NHR₄ and -NR₄R₅ groups in which R₄ and R₅ are, independently of each other, linear or branched, saturated or unsaturated hydrocarbon radicals containing 1 to 6 carbon atoms, with the proviso that the total number of carbon atoms in R₄ + R₅ does not exceed 7, the said R₄ and R₅ optionally being substituted with a halogen atom selected from the group consisting of iodine, bromine, chlorine and fluorine; a hydroxyl (-OH); sulfonic (-SO₃⁻), sulfate (-SO₄⁻); phosphate (-PO₄H₂); primary amine (-NH₂); secondary amine

(-NHR₁), tertiary amine (-NR₁R₂) and/or quaternary amine (-N⁺R₁R₂R₃) group with R₁, R₂ and R₃ being, independently of each other, a linear or branched, saturated or unsaturated hydrocarbon radical containing 1 to 6 carbon atoms, with the proviso that the sum of the carbon atoms of R₄ + R₅ + R₁ + R₂ + R₃ does not exceed 7;

- maleic anhydride;
- itaconic acid;
- vinyl alcohol of formula CH₂=CHOH;
- vinyl acetate of formula CH₂=CH-OCOCH₃;
- N-vinyl lactams;
- vinyl ethers of formula CH₂=CHOR₆ in which R₆ is a linear or branched, saturated or unsaturated hydrocarbon radical containing from 1 to 6 carbons atoms;
- water-soluble styrene derivatives;
- dimethyldiallylammonium chloride; and
- vinylacetamide.

31. (Withdrawn) The dispersion as claimed in claim 25, in which the water-soluble units are totally or partially of one or more of the following components:

- water-soluble polyurethanes,
- xanthan gum,
- alginates and derivatives thereof,
- cellulose derivatives,
- galactomannans and derivatives thereof, and
- polyethyleneimine.

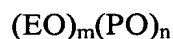
32. (Previously Presented) The dispersion as claimed in claim 25, in which the water-soluble units have a molar mass ranging from 1000 g/mol to 5 000 000 g/mol when

they constitute the water-soluble backbone of a grafted polymer, or a molar mass ranging from 500 g/mol to 100 000 g/mol when they constitute a block of a multiblock polymer or when they constitute the grafts of a grafted polymer.

33. (Previously Presented) The dispersion as claimed in claim 25, in which the units with an LCST are one or more of the following polymers:

- polyethers,
- polyvinyl methyl ethers,
- polymeric and copolymeric N-substituted acrylamide derivatives with an LCST and
- polyvinylcaprolactam and vinylcaprolactam copolymers.

34. (Withdrawn) The dispersion as claimed in claim 25, in which the units with an LCST are polypropylene oxide (PPO)_n with n=10 to 50, or random copolymers of ethylene oxide (EO) and of propylene oxide (PO), represented by the formula:

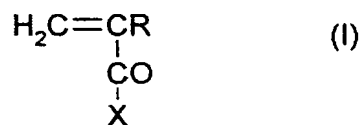


in which m is an integer ranging from 1 to 40 and n is an integer ranging from 10 to 60.

35. (Withdrawn) The dispersion as claimed in claim 34, in which the molar mass of the units with an LCST is from 500 to 5300 g/mol.

36. (Previously Presented) The dispersion as claimed in claim 33, in which the units with an LCST are polymeric or copolymeric N-isopropylacrylamide or N-ethylacrylamide derivatives and the molar mass of these units with an LCST is from 1000 g/mol to 50 000 g/mol.

37. (Withdrawn) The dispersion as claimed in claim 25, in which the units with an LCST are a polyvinylcaprolactam or a copolymer of vinylcaprolactam and of a vinyl monomer corresponding to formula (I)



in which:

- R is chosen from H, -CH₃, -C₂H₅ or -C₃H₇, and
- X is chosen from:
- alkyl oxides of -OR' type in which R' is a linear or branched, saturated or unsaturated hydrocarbon radical containing from 1 to 6 carbon atoms, optionally substituted with at least one halogen atom (selected from the group consisting of iodine, bromine, chlorine and fluorine); a sulfonic (-SO₃⁻), sulfate (-SO₄⁻), phosphate (-PO₄H₂); hydroxyl (-OH); primary amine (-NH₂); secondary amine (-NHR₁), tertiary amine (-NR₁R₂) or quaternary amine (-N⁺R₁R₂R₃) group with R₁, R₂ and R₃ being, independently of each other, a linear or branched, saturated or unsaturated hydrocarbon radical containing 1 to 6 carbon atoms, with the proviso that the sum of the carbon atoms of R' + R₁ + R₂ + R₃ does not exceed 7; and
- -NH₂, -NHR₄ and -NR₄R₅ groups in which R₄ and R₅ are, independently of each other, linear or branched, saturated or unsaturated hydrocarbon radicals containing 1 to 6 carbon atoms, with the proviso that the total number of carbon atoms in R₄ + R₅ does not exceed 7, the said R₄ and R₅ optionally being substituted with a halogen atom (selected from the group consisting of iodine, bromine, chlorine and fluorine); a hydroxyl (-OH); sulfonic (-SO₃⁻), sulfate (-SO₄⁻); phosphate (-PO₄H₂); primary amine (-NH₂); secondary amine (-NHR₁), tertiary amine (-NR₁R₂) and/or quaternary amine (-N⁺R₁R₂R₃) group with R₁, R₂ and R₃ being, independently of each other, a

linear or branched, saturated or unsaturated hydrocarbon radical containing 1 to 6 carbon atoms, with the proviso that the sum of the carbon atoms of $R_4 + R_5 + R_1 + R_2 + R_3$ does not exceed 7;

or of a monomer chosen from maleic anhydride, itaconic acid, vinylpyrrolidone, styrene and its derivatives, dimethyldiallylammonium chloride, vinylacetamide, vinyl alcohol, vinyl acetate, vinyl ethers and vinyl acetate derivatives.

38. (Withdrawn) The dispersion as claimed in claim 37, in which the molar mass of the units with an LCST is from 1000 to 500 000 g/mol.

39. (Previously Presented) The dispersion as claimed in claim 25, in which the proportion by mass of units with an LCST in the polymer is from 5 to 70% relative to the polymer.

40. (Previously Presented) The dispersion as claimed in claim 25, in which the demixing temperature of the units with an LCST is from 10 to 35°C, for a concentration in water of 1% by mass of the units with an LCST.

41. (Previously Presented) The dispersion as claimed in claim 25, in which the concentration by mass of polymer in the aqueous phase is from 0.01 to 20%.

42. (Previously Presented) The dispersion as claimed in claim 25, in which the polymer is such that an aqueous solution of this polymer at 2% by weight has a gel point of from 5 to 40°C.

43. (Previously Presented) The dispersion as claimed in claim 25, in which the oily phase comprises at least one oil selected from the group consisting of hydrocarbon-based animal oils, hydrocarbon-based plant oils, synthetic esters, synthetic ethers, linear hydrocarbons, branched hydrocarbons, essential oils, fatty alcohols, fluoro oils, silicone oils, and mixtures thereof.

44. (Previously Presented) The dispersion as claimed in claim 25, further comprising one or more adjuvants.

45. (Previously Presented) The dispersion as claimed in claim 25, which is in the form of a cosmetic make-up or care composition.

46. (Withdrawn) A process of making up facial skin and/or body skin, mucous membranes (lips), the scalp and/or keratin fibres, comprising applying the dispersion as claimed in claim 25 to said facial skin and/or body skin, mucous membranes (lips), the scalp and/or keratin fibres.

47. (Withdrawn) A process for treating and/or caring for human keratin materials, comprising applying a dispersion as claimed in claim 25 the keratin materials.

48. (Withdrawn) A method of stabilizing a dispersion, comprising adding a polymer comprising water-soluble units and units with an LCST, to the aqueous phase of the dispersion wherein the dispersion comprises at least one aqueous phase and at least one oily phase, and wherein the polymer stabilizes the dispersion when the dispersion is subjected to temperature variations from 4 to 50°C.

49. (Previously Presented) The dispersion as claimed in claim 25, wherein the polymer is in the form of a block polymer in the form of a grafted polymer whose backbone is formed from water-soluble units and bears grafts consisting of units with an LCST and which is partially crosslinked.

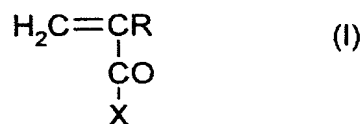
50. (Previously Presented) The dispersion as claimed in claim 30, wherein the at least one monomer is an N-vinyl lactam and is selected from the group consisting of N-vinylpyrrolidone, N-vinylcaprolactam and N-butyrolactam.

51. (Previously Presented) The dispersion as claimed in claim 31, wherein at least one component is an alginate derivative which is propylene glycol alginate.

52. (Previously Presented) The dispersion as claimed in claim 31, wherein at least one component is a galactomannan derivative selected from the group consisting of konjac gum, guar gum, hydroxypropylguar, hydroxypropylguar modified with sodium methylcarboxylate groups, and hydroxypropyltrimethylammonium guar chloride.

53. (Previously Presented) The dispersion as claimed in claim 33, wherein at least one polymer is a polyether which is selected from the group consisting of polyethylene oxide (PEO), polypropylene oxide (PPO) and random copolymers of ethylene oxide (EO) and of propylene oxide (PO).

54. (Previously Presented) The dispersion as claimed in claim 33, wherein at least one polymer is polymeric and copolymeric N-substituted acrylamide derivatives with an LCST and is one or more of poly-N-isopropyl acrylamide, poly-N-ethylacrylamide and copolymers of N-isopropylacrylamide or of N-ethylacrylamide and of a vinyl monomer corresponding to formula (I)



in which:

- R is chosen from H, -CH₃, -C₂H₅ or -C₃H₇, and
- X is chosen from:
- alkyl oxides of -OR' type in which R' is a linear or branched, saturated or unsaturated hydrocarbon radical containing from 1 to 6 carbon atoms, optionally substituted with at least one halogen atom selected from the group consisting of iodine, bromine, chlorine, and fluorine; a sulfonic (-SO₃⁻), sulfate (-SO₄⁻), phosphate (-PO₄H₂); hydroxyl (-OH); primary amine (-NH₂); secondary amine (-NHR₁), tertiary amine (-NR₁R₂) or quaternary amine (-

$N^+R_1R_2R_3$) group with R_1 , R_2 and R_3 being, independently of each other, a linear or branched, saturated or unsaturated hydrocarbon radical containing 1 to 6 carbon atoms, with the proviso that the sum of the carbon atoms of $R' + R_1 + R_2 + R_3$ does not exceed 7; and

- $-NH_2$, $-NHR_4$ and $-NR_4R_5$ groups in which R_4 and R_5 are, independently of each other, linear or branched, saturated or unsaturated hydrocarbon radicals containing 1 to 6 carbon atoms, with the proviso that the total number of carbon atoms in $R_4 + R_5$ does not exceed 7, the said R_4 and R_5 optionally being substituted with a halogen atom selected from the group consisting of iodine, bromine, chlorine and fluorine; a hydroxyl ($-OH$); sulfonic ($-SO_3^-$), sulfate ($-SO_4^-$); phosphate ($-PO_4H_2$); primary amine ($-NH_2$); secondary amine ($-NHR_1$), tertiary amine ($-NR_1R_2$) and/or quaternary amine ($-N^+R_1R_2R_3$) group with R_1 , R_2 and R_3 being, independently of each other, a linear or branched, saturated or unsaturated hydrocarbon radical containing 1 to 6 carbon atoms, with the proviso that the sum of the carbon atoms of $R_4 + R_5 + R_1 + R_2 + R_3$ does not exceed 7;

or of a monomer chosen from maleic anhydride, itaconic acid, vinylpyrrolidone, styrene and its derivatives, dimethyldiallylammonium chloride, vinylacetamide, vinyl ethers and vinyl acetate derivatives.

55. (Previously Presented) The dispersion as claimed in claim 44, wherein the one or more adjuvants are selected from the group consisting of mineral fillers, organic fillers, surfactants, hydrophilic active agents, lipophilic active agents, preserving agents, gelling agents, plasticizers, antioxidants, fragrances, odor absorbers, antifoams, sequestering agents, pH adjusters, buffers and dyestuffs.

56. (Previously Presented) The dispersion as claimed in claim 30, wherein the at least one monomer is a water-soluble styrene derivative, which is styrene sulfonate.

57. (Previously Presented) The dispersion as claimed in claim 31, wherein at least one component is a cellulose derivative and which is selected from the group consisting of carboxymethylcellulose, hydroxypropylcellulose, hydroxyethylcellulose and quaternized hydroxyethylcellulose.

58. (Previously Presented) The dispersion as claimed in claim 34, wherein m is an integer of from 2 to 20.

59. (Previously Presented) The dispersion as claimed in claim 34, wherein n is an integer of from 20 to 50.

60. (Previously Presented) The dispersion as claimed in claim 35, wherein the molar mass of the units with an LCST is from 1500 to 4000 g/mol.

61. (Previously Presented) The dispersion as claimed in claim 36, wherein the molar mass of the units with an LCST is from 200 to 50 000 g/mol.

62. (Previously Presented) The dispersion as claimed in claim 38, wherein the molar mass of the units with an LCSt is from 2000 to 50 000 g/mol.

63. (Previously Presented) The dispersion as claimed in claim 39, wherein the proportion by mass of units with an LCST in the polymer is from 20 to 65% relative to the polymer.

64. (Previously Presented) The dispersion as claimed in claim 39, wherein the proportion by mass of units with an LCST in the polymer is from 30 to 60 % relative to the polymer.

65. (Previously Presented) The dispersion as claimed in claim 41, wherein the concentration by mass of polymer in the aqueous phase is from 0.1 to 10%.

66. (Previously Presented) The dispersion as claimed in claim 42, wherein the polymer is such that an aqueous solution of this polymer at 2% by weight has a gel point of from 10 to 35°C.

67. (Previously Presented) The dispersion as claimed in claim 45, wherein the cosmetic make-up or care composition is in the form suitable for being applied to at least one of the skin, the scalp, the nails, the hair, the eyelashes, the eyebrows, the eyes, mucous membranes, semi-mucous membranes, and other area of body or facial skin.

68. (Previously Presented) The dispersion as claimed in claim 30, wherein the water-soluble units are (meth)acrylic acid.

69. (Previously Presented) The dispersion as claimed in claim 33, wherein the units with an LCST are polymeric and copolymeric N-substituted acrylamide derivatives with an LCST.

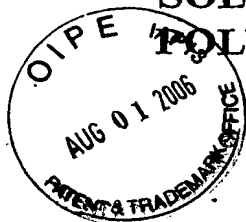
APPENDIX II (EVIDENCE)

- (1) The specification on page 2, line 6- page 2, line 2.
- (2) The specification on page 4, line 25 to page 5, line 31.
- (3) The specification on page 32, line 20 through page 34, line 14.
- (4) The specification on page 27, Table 1.
- (5) The specification on page 34, line 16 through page 36, line 5.
- (6) Malcolm and Rowlinson publication (1957), entered into the record on March 4, 2005.
- (7) Dow Corning Technical Sheet: Propylene glycol, entered into the record on March 4, 2005.

RELATED PROCEEDINGS APPENDIX

An appeal will be or has been filed in U.S. application serial no. 10/069,983, a case that is related to the present application.

THE THERMODYNAMIC PROPERTIES OF AQUEOUS SOLUTIONS OF POLYETHYLENE GLYCOL, POLYPROPYLENE GLYCOL AND DIOXANE



BY G. N. MALCOLM * AND J. S. ROWLINSON
Dept. of Chemistry, University of Manchester

Received 7th March, 1957

Measurements are reported of the vapour pressures, the heats of mixing, the densities and the phase relationships of solutions of polyethylene glycol and polypropylene glycol in water. The free energies, heats and entropies of dilution, the volume changes on mixing and the excess partial volumes have been derived. The results show significant differences from those for other polar polymer solutions. A comparison is made with the results for aqueous solutions of dioxane which is the cyclic dimer of the repeating unit in polyethylene glycol. Some new measurements of the vapour pressures of dioxane + water solutions at temperatures between 100° C and 156° C and of the heat of mixing at 25° C, are reported in an appendix.

Few precise measurements have yet been made of the thermodynamic properties of polymer solutions which contain polar molecules. This paper reports the results of a detailed investigation of the properties of the solutions of polyethylene glycol and polypropylene glycol in water. These solutions provide examples of polymer solutions in which association and clustering of solvent molecules may occur and in which orientation-dependent interactions are present between solvent and polymer. Polyethylene glycol and polypropylene glycol were chosen because they are the simplest available polyethers. Several other polyethers are in course of preparation for future study.

EXPERIMENTAL

MATERIALS.—Samples of polyethylene and polypropylene glycols were kindly supplied by Oxirane Ltd. of Manchester. The number average molecular weights were given as 5000, 3000, 1500 and 300 for the polyethylene glycols and 750 and 400 for the polypropylene glycols. The solid samples were purified before use by reprecipitation with hexane from hot carbon tetrachloride solution. All the samples were carefully dried under high vacuum.

VAPOUR PRESSURE MEASUREMENTS.—The difference between the vapour pressure of the solution and that of pure water at the same temperature was measured with a mercury manometer in an apparatus similar to that used by Taylor and Rowlinson.¹ Times of up to 36 h were necessary for the pressure differences to become steady. The constancy of the thermostat was ± 0.01 deg. at 25° C and ± 0.04 deg. at 65° C. The thermometers were calibrated against thermometers standardized by the N.P.L. A correction for the vapour space was applied when calculating the concentrations. Measurements of the vapour pressure of water made with this apparatus agreed well with those recommended by Dorsey.²

HEAT OF MIXING MEASUREMENTS.—These were performed in an isothermal naphthalene calorimeter, which was a much enlarged version of the instrument described by Beynon and Humphries.³ The central tube of the calorimeter was made 2 in. wide and 20 in. long. The lower 6 in. of this tube were separated from the rest by an evacuated B 55 ground glass stopper. A thin central tube through the stopper allowed two nylon threads to pass to the mixing vessel inside the reaction chamber. Two additional heat reflecting

* present address : Otago University, Dunedin, New Zealand.

shields were added to those described by Beynon and Humphries. One of these was an aluminium foil sheet placed on the bottom face of the glass stopper. The other was a polished brass disc which was fixed immediately above the stopper and was heated electrically to maintain it at the temperature of the thermostat.

The mixing vessel, shown in fig. 1, was a glass sphere of 4 cm diameter divided into two compartments by an inner tube and a layer of mercury. When solid polymer material was used it was placed in the outer compartment, O, melted, solidified and weighed.

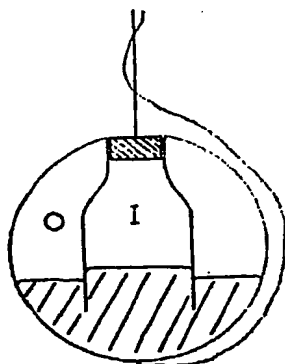


FIG. 1.—Mixing vessel.

Mercury was added completely to fill the outer compartment, and the requisite amount of water was then added to the inner compartment, I, from a weight burette. Liquid polymer material was placed on top of mercury in the outer compartment by means of a hypodermic syringe, and the water was then added as before. The vessel was closed by means of a tightly fitting rubber bung so that no vapour space remained. The bung was initially inserted well inside the vessel so that the slight expansion of the contents which occurred on heating up to 80° C was taken up by allowing the bung to be driven upwards until it pressed against a strong wire fastened round the vessel. Mixing and stirring were achieved by repeatedly tipping the vessel upside down by means of the nylon threads. The movement of the mercury served both to stir the solution and also to conduct the heat of mixing rapidly to the outer wall of the vessel. From there the heat was conducted by a silicone oil to the wall of the naphthalene chamber. (The level of the oil in the

reaction chamber was always below the top of the naphthalene chamber.) The movement of the mercury in the capillary was measured with a cathetometer.

The sensitivity of the calorimeter was 1.544 ± 0.007 cm/cal (1 cal = 4.1840 joules). This figure gave a value of 0.00429 cm³/cal for the volume change of naphthalene on fusion, which agreed well with the values 0.00427 and 0.00433 cm³/cal recorded by Beynon and Humphries for their work and that of Coffin.⁴ The apparatus was placed in a bath which could be maintained at constant temperature to within $\pm 0.001^\circ$ C for periods of several hours. During an experiment variations in the rate of background drift of the mercury in the capillary tube were not more than 0.001 cm/sec. In each experiment amounts of the order of 1 to 6 g of each substance were used, and were chosen so that between 20 and 40 cal were evolved on mixing (except in the regions of extreme dilution or concentration). The time of a complete mixing experiment was usually 90 min, so that the maximum error which could be caused by change in the rate of background drift was 0.6 %.

DENSITY MEASUREMENTS.—The densities of the solutions were measured in a bi-capillary pyknometer, which was filled by means of a hypodermic syringe. The pyknometer was calibrated at each temperature with distilled water.

PHASE SEPARATION MEASUREMENTS.—These were carried out by heating the solutions in Pyrex tubes. Each tube contained a short length of glass rod to aid stirring, and after filling with solution, was frozen, evacuated and sealed off. Heating up to 250° C was carried out in an oil bath. The temperature of incipient phase separation was first noted as the bath was slowly warmed (or cooled), and was compared with the temperature at which the solution first became clear again. Readings up to 150° C could be reproduced to within $\pm 0.1^\circ$ C, those up to 200° C to $\pm 1^\circ$ C and above 200° C to $\pm 2^\circ$ C.

RESULTS

VAPOUR PRESSURE MEASUREMENTS

The vapour pressures and the solvent activities as functions of the polymer weight fraction are shown in tables 1 and 2.

The experimental error in the measured pressure differences is thought to be within $\pm 1\%$, and the error in the weight fractions is less than this amount. The vapour pressure values for water used in the calculation of the activities are those recommended by Dorsey.² Correction for the imperfection of the vapour was made using the equation of state of Keyes, Smith and Gerry.²

For all four solutions the vapour pressure isotherms are everywhere convex towards the vapour pressure axis. In this respect they differ from the isotherms for the nitro-cellulose + ketone systems⁵ and the agar-agar + water system,⁶ which have sigmoid

shapes. The vapour pressure curves were not dependent on whether the water concentration was being increased or decreased; that is, there was no hysteresis.

TABLE 1.—THE VAPOUR PRESSURES IN mm Hg (AT 0° C) OF AQUEOUS SOLUTIONS OF POLYETHYLENE GLYCOL

temp. °C	wt. fraction of polymer (W_2)	vapour pressure (p_1)	activity of solvent (a_1)	wt. fraction of polymer (W_2)	vapour pressure (p_1)	activity of solvent (a_1)
MOLECULAR WEIGHT 5000						
65.00	0.990	35.71	0.191	0.835	150.73	0.805
	0.970	78.92	0.422	0.764	160.58	0.857
	0.951	102.31	0.547	0.735	165.62	0.884
	0.949	103.24	0.552	0.662	171.30	0.914
	0.902	132.48	0.708	0.496	182.79	0.974
	0.900	133.11	0.711	0.000	187.54	1.000
	0.839	150.33	0.803			
60.00	0.950	81.50	0.547	0.735	130.91	0.877
	0.902	104.22	0.699	0.000	149.38	1.000
	0.835	118.70	0.796			
MOLECULAR WEIGHT 3000						
65.00	0.990	34.36	0.184	0.846	145.01	0.774
	0.970	75.03	0.402	0.765	158.70	0.847
	0.950	99.26	0.531	0.704	166.34	0.888
	0.904	127.01	0.679	0.499	181.72	0.969
	0.897	130.46	0.697	0.000	187.54	1.000
55.00	0.970	47.10	0.400	0.702	102.62	0.871
	0.950	61.74	0.524	0.499	113.76	0.964
	0.844	89.45	0.759	0.000	118.04	1.000
MOLECULAR WEIGHT 300						
65.00	0.988	24.97	0.134	0.662	156.12	0.833
	0.951	63.95	0.342	0.489	173.54	0.926
	0.900	97.13	0.520	0.299	181.89	0.970
	0.801	132.31	0.707	0.000	187.54	1.000
50.00	0.988	12.12	0.132	0.660	75.58	0.818
	0.950	30.31	0.329	0.488	84.77	0.917
	0.899	46.07	0.499	0.298	89.39	0.966
	0.800	63.11	0.683	0.000	92.51	1.000
30.00	0.988	3.95	0.124	0.659	25.10	0.789
	0.950	9.81	0.309	0.488	28.65	0.900
	0.899	14.88	0.468	0.298	30.41	0.956
	0.800	20.61	0.648	0.000	31.82	1.000

TABLE 2.—THE VAPOUR PRESSURE IN mm Hg (AT 0° C) OF AQUEOUS SOLUTIONS OF POLYPROPYLENE GLYCOL 400

temp. °C	wt. fraction of polymer (W_2)	vapour pressure (p_1)	activity of solvent (a_1)	wt. fraction of polymer (W_2)	vapour pressure (p_1)	activity of solvent (a_1)
50.00	0.990	19.90	0.216	0.701	90.99	0.984
	0.952	59.13	0.640	0.591	91.68	0.991
	0.902	78.94	0.854	0.000	92.51	1.000
	0.801	89.05	0.963			
30.00	0.990	6.62	0.208	0.700	31.12	0.978
	0.950	19.88	0.625	0.590	31.36	0.985
	0.901	26.89	0.845	0.000	31.82	1.000
	0.800	30.40	0.955			

CALOMETRIC MEASUREMENTS

The heat of mixing results are recorded in table 3.

TABLE 3.—THE HEATS OF MIXING AT 80.3° C FOR AQUEOUS SOLUTIONS OF POLYETHYLENE GLYCOL IN cal/g OF MIXTURE AS A FUNCTION OF THE WEIGHT FRACTION OF POLYMER (W_2)

W_2	$-\Delta H$ cal/g	W_2	$-\Delta H$ cal/g
MOLECULAR WEIGHT 5000			
0.206	4.79	0.755	4.89
0.336	7.03	0.825	3.25
0.480	8.20	0.887	1.39
0.548	7.91	0.953	0.30
0.675	6.18		
MOLECULAR WEIGHT 3000			
0.102	2.32	0.780	4.66
0.303	6.59	0.847	2.87
0.517	8.14	0.904	1.33
0.719	5.92		
MOLECULAR WEIGHT 300			
0.287	6.29	0.820	5.26
0.475	8.05	0.897	3.10
0.630	7.44	0.948	1.42
0.719	6.59		

The probable error in the heat of mixing per gram of mixture is $\pm 2\%$. A comparison between these results and those for the dioxane + water system (see appendix) is made in fig. 2.

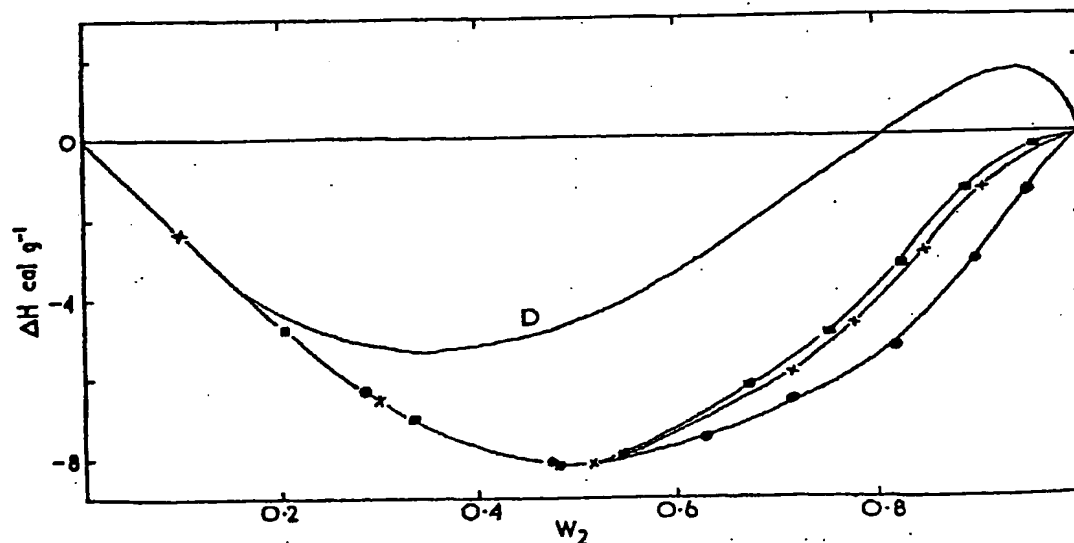


FIG. 2.—Heats of mixing at 80.3° C of polyethylene glycol and water plotted against weight fraction of polymer. Squares, mol. wt. 5000; crosses, mol. wt. 3000; circles, mol. wt. 300. Curve D, dioxane and water (20° C).

THERMODYNAMIC DILUTION FUNCTIONS

The results in tables 1-3 were used to calculate free energies and heats of dilution for the four solutions. For the three polyethylene glycol solutions the free energies of dilution at 65° C and the heats of dilution at 80.3° C were combined to give approximate values of the entropies of dilution. (The heats of dilution calculated at several temperatures from the vapour pressure measurements indicate that the temperature coefficient of the heat of dilution is small and positive.) For the polypropylene glycol solutions the heats of dilution were calculated from the vapour pressure measurements, and are the mean

FIG. 3.—Thermodynamic dilution functions plotted against weight fraction of polymer or dioxane (see text). A and B, polyethylene glycols 5000 and 300; C, polypropylene glycol 400; D, dioxane.

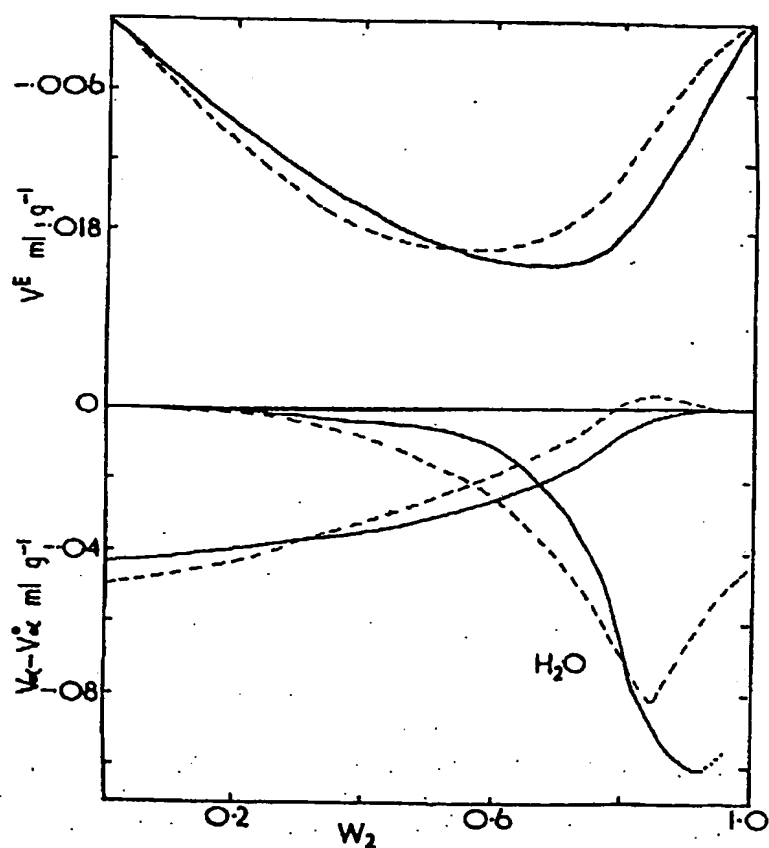
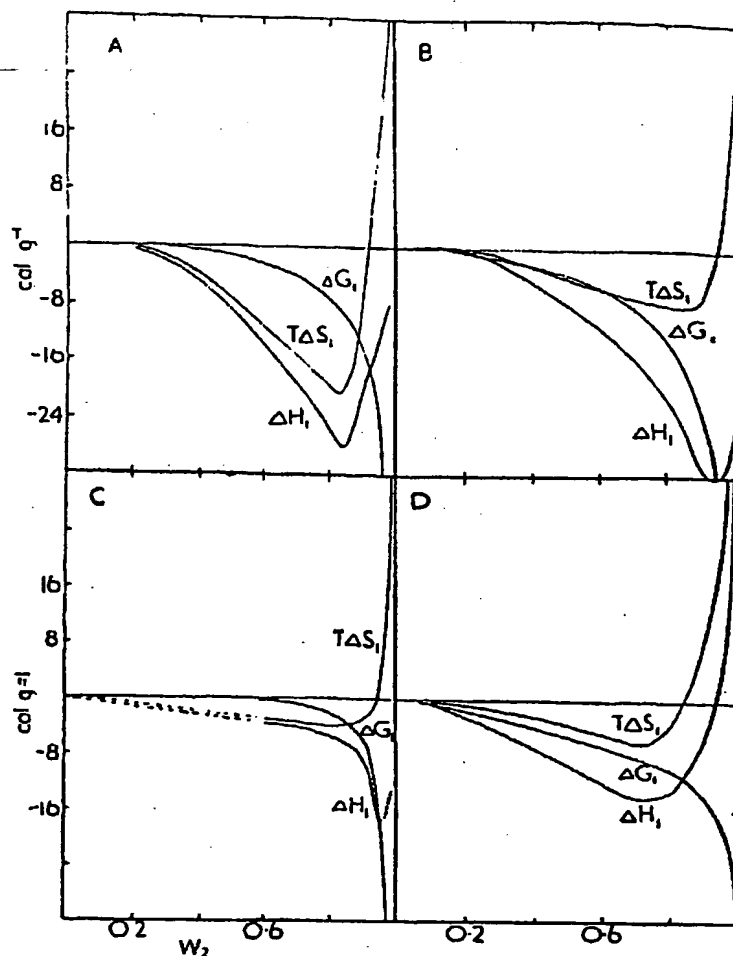


FIG. 4.—Excess volumes and excess partial volumes as functions of weight fraction of polymer or dioxane. Full lines, polyethylene glycol 5000 at 65° C; broken lines, dioxane at 25° C.

values between 30° C and 50° C. The smoothed values of the three dilution functions are plotted in fig. 3. Fig. 3(d) shows the dilution functions for the dioxane + water system calculated from vapour pressures at 25° C and heats of mixing at 20° C (see appendix). The curves for the solution of polyethylene glycol 3000 are very similar to those for the sample of molecular weight 5000, and are not plotted in the figure.

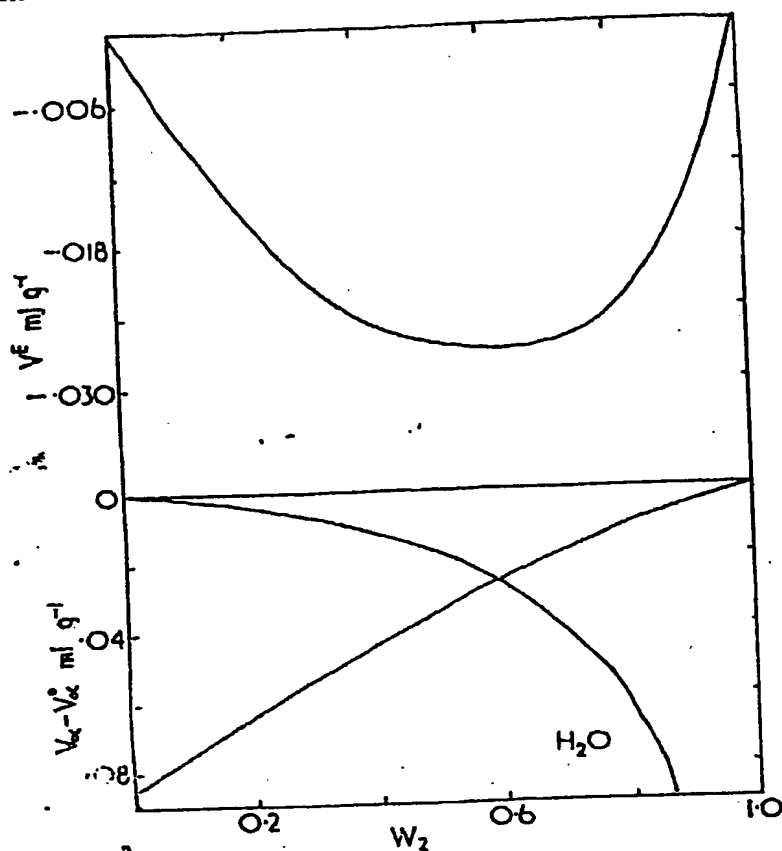
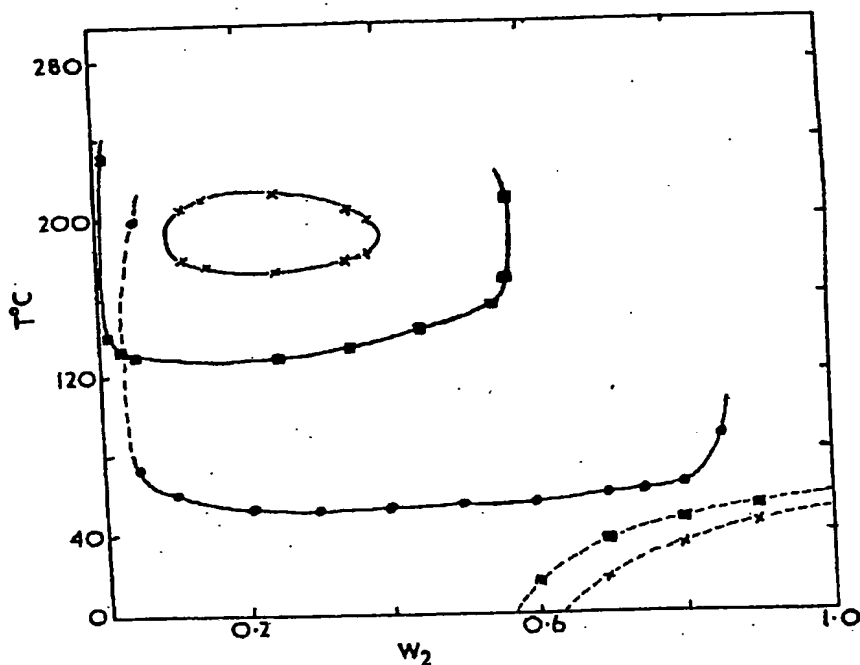


FIG. 5.—Excess volumes and excess partial volumes in solutions of polypropylene glycol 400 at 50° C as functions of the weight fraction of polymer.

FIG. 6.—Phase diagram for aqueous solutions of polyethylene and polypropylene glycols. Squares and crosses, polyethylene glycols 5000 and 3000; circles, polypropylene glycol 400. Lower right-hand curves, solid-liquid boundaries.



VOLUME CHANGES ON MIXING

The densities of the solutions of the three polyethylene glycols plotted against composition fell on the same smooth curve. The results were used to calculate the excess volume of the mixture and the excess partial volumes of the components. These functions

are plotted in fig. 4, together with the corresponding results for the dioxane + water solution (see appendix). The results for the polypropylene glycol solutions are shown in fig. 5.

PHASE RELATIONSHIPS

The phase diagrams which were obtained are shown in fig. 6. No phase separation was observed in the solutions of polyethylene glycol 300 or dioxane.

DISCUSSION

Analysis of the results for the solution of polyethylene glycol 5000 in terms of the free energy equation

$$\Delta G_1 = RT\{\ln(1 - \phi_2) + \phi_2 + \chi\phi_2^2\} \quad (1)$$

gives values of the parameter χ which increase uniformly with volume fraction of polymer (ϕ_2) from 0.4 at $\phi_2 = 0.25$ to 0.75 at $\phi_2 = 0.66$, and then increase more rapidly to 1.24 at $\phi_2 = 0.9$.

For the nitrocellulose + ketone systems and the agar-agar + water solution the values of χ decreased with increase in ϕ_2 and were negative at high concentrations of polymer. This difference in behaviour is further illustrated by the fact that the vapour pressure isotherms of the solutions studied here are not sigmoid in shape like those of the nitrocellulose and agar-agar solutions.

Examination of the thermodynamic dilution functions is interesting in this connection. For the solution of polyethylene glycol 5000 the excess of the entropy and heat of dilution over the values predicted by the equations,

$$\Delta S_1 = -R\{\ln(1 - \phi_2) + \phi_2\}, \quad (2)$$

and

$$\Delta H_1 = 0, \quad (3)$$

have been calculated, and are plotted with the corresponding free energy quantity in fig. 7.

(For convenience in the following discussion the differences between the observed dilution functions and those given by eqn. (2) and (3) are called "excess" dilution functions.) From fig. 7 it is apparent that the "excess" entropy of dilution determines the sign of the "excess" free energy, and makes it positive despite the negative heat of dilution. Consequently the values of the parameter χ in eqn. (1) are positive. In the agar-agar + water system at high polymer concentrations the negative "excess" entropy of dilution is numerically less than the exothermic heat of dilution, so that the "excess" free energy in this region is negative and gives negative values of χ . No entropy or heat of dilution values are yet available for the nitrocellulose solutions.

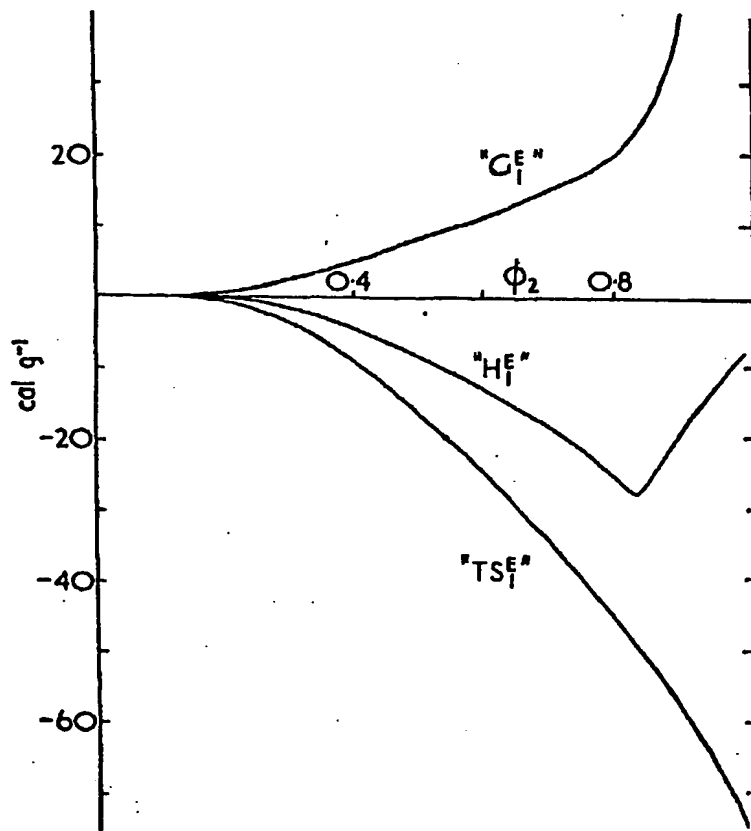


FIG. 7.—"Excess" thermodynamic dilution functions for the solution of polyethylene glycol 5000 (see text). G_1^E and TS_1^E at 65° C, H_1^E at 80.3° C.

Fig. 7 reveals that the much greater increase in the value of X which was found in the region of high polymer concentration results from the sudden change in slope of the heat of dilution curve, which passes through a minimum. Similar behaviour in the heat of dilution is found in the dioxane + water system (fig. 3D) and in the ethanol + water system.⁷ The vapour pressure results for the solution of polypropylene glycol suggest that the same behaviour is present there (fig. 3C).

The appearance of lower consolute temperatures in the solutions of the higher polyethylene glycols is another indication that negative entropies are determining the solution behaviour. Lower consolute temperatures have seldom been observed in polymer solutions.

The heat of mixing results in fig. 2 reveal marked differences in the behaviour of polymer molecules which seemingly differ only in chain length. It might reasonably have been anticipated that the dioxane curve would lie below that for the lowest polymer, since it contains only two ethylene oxide units. But the observed heats of mixing are in the same sequence as the proportions by weight of hydroxyl end groups in the various molecules, so that it seems probable that the end groups are responsible for the differences in behaviour. This hypothesis is supported by the results of some simple test-tube experiments with two related substances, ethylene glycol dimethyl ether and ethylene glycol monomethyl ether. The heat of mixing for the first of these substances, which contains no hydroxyl group, was positive for low water concentrations and became negative when the weight fraction of water reached 0.15. Addition of small quantities of water to the monomethyl ether resulted in a negative heat of mixing of a similar magnitude to that observed in the concentrated solutions of polyethylene glycol 300.

We wish to thank Prof. Gee for suggesting this work and for discussion of the results. We are grateful to Dr. A. J. Lowe of Oxirane for information concerning the polymers. One of us (G. N. M.) acknowledges with thanks the award of an Overseas Scholarship from New Zealand by the Royal Commission for the Exhibition of 1951.

APPENDIX

THE SYSTEM DIOXANE + WATER

(with A. Davis)

The vapour pressures of aqueous solutions of dioxane have been measured by Hovorka, Schaeffer and Dreisbach⁸ (0–80° C), by Vierk⁹ (25° C) and by Bacarella, Finch and Grunwald¹⁰ (25° C). Vierk has also measured the heat of mixing at 20° C and Stallard and Amis¹¹ the heat capacity at 40° C. The densities have been measured, amongst others, by Hovorka, Schaeffer and Dreisbach and by Griffiths,¹² both of whom calculate the partial molar volumes at 25° C. These measurements show clearly that at room temperature this system has a positive excess Gibbs free energy, a negative excess enthalpy and a negative excess volume in mixtures weak in dioxane. This is the behaviour of solutions which show lower consolute points. We have therefore analysed these measurements further and have supplemented them with measurements of the vapour pressure up to 156° C and a search for such a consolute point up to 240° C.

PREVIOUS MEASUREMENTS.—We have disregarded the vapour pressures of Hovorka, Schaeffer and Dreisbach as their partial pressures at 25° C do not satisfy the Gibbs-Duhem equation and their total pressures are not in agreement with those of Bacarella, Finch and Grunwald. The partial pressures and activities of Vierk are satisfactory and lead to the excess free energy shown in fig. 8. The measurements of Bacarella, Finch and Grunwald are all at mole fractions of dioxane of less than 0.33. They give GE about 3 % larger than that of Vierk.

The heat of mixing measured by Vierk at 20° C (fig. 8) has been confirmed by the three new measurements at 25° C reported below. The excess heat capacity of the system has been calculated from the measurements of Stallard and Amis and is shown in fig. 9.

The densities of Hovorka and of Griffiths at 25° C agree and lead to the excess volume shown in fig. 10. Griffiths' measurements will not support the impossible discontinuities which he has reported in the partial molar volume at mole fractions of dioxane between 0.4 and 0.8.

FIG. 8.—Excess free-energy and enthalpy as a function of mole fraction of dioxane. Curve 1, GE from Vierk⁹ (25° C); curve 2, GE from Bacarella, Finch and Grunwald¹⁰ (25° C); curve 3, HE from Vierk⁹ (20°) circles, and present measurements (25° C) triangles.

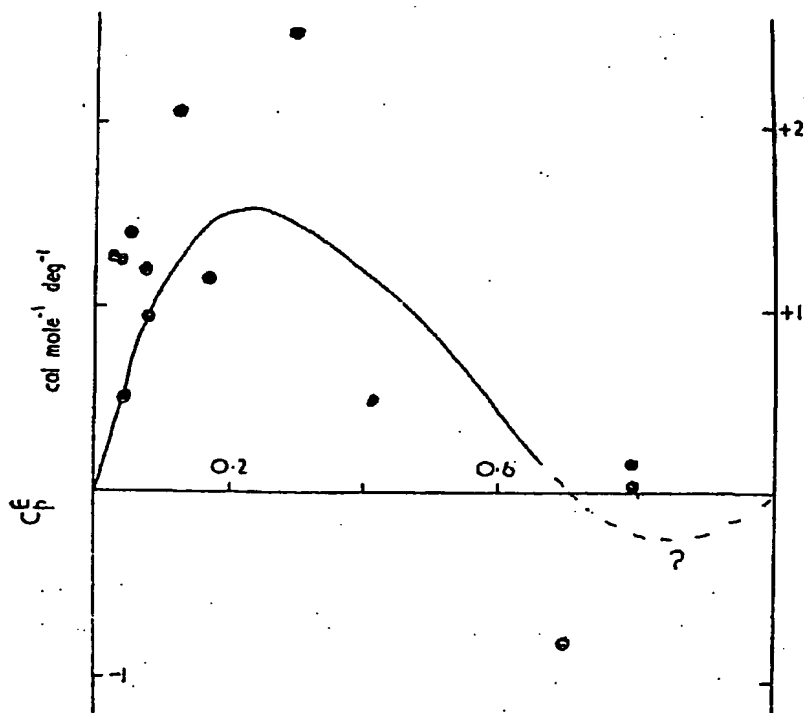
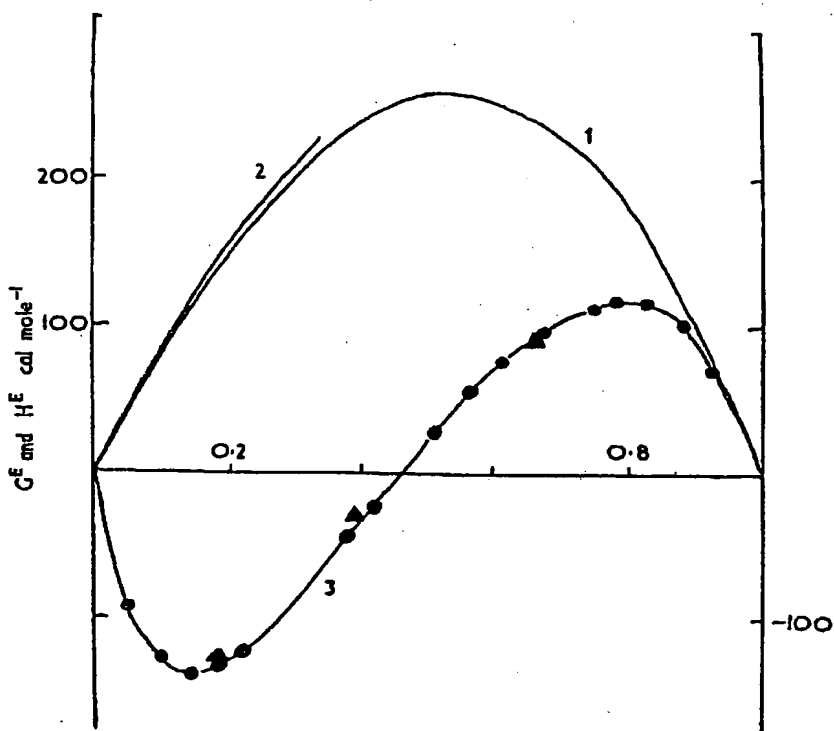


FIG. 9.—Excess heat capacity at 40° C as a function of the mole fraction of dioxane, from Stallard and Amis.¹¹

PRESENT MEASUREMENTS.—A.R. dioxane was fractionally distilled and refluxed with liquid sodium. The dioxane was shown to be completely dry and free from all substances containing active hydrogen by the immediate formation of a coloured complex on adding a little fluorenone.¹³ The dioxane, containing a small amount of complex in solution, was stored *in vacuo*. Mixtures were made up by weight by distillation of the de-gassed components into evacuated tubes fitted with glass break-seals.

The vapour pressures were measured by observing on a mercury manometer the pressure differences between the mixtures and pure water. Tubes containing the mixture and the water were heated in a vapour thermostat. The vapour pressures of water were those recommended by Dorsey.²

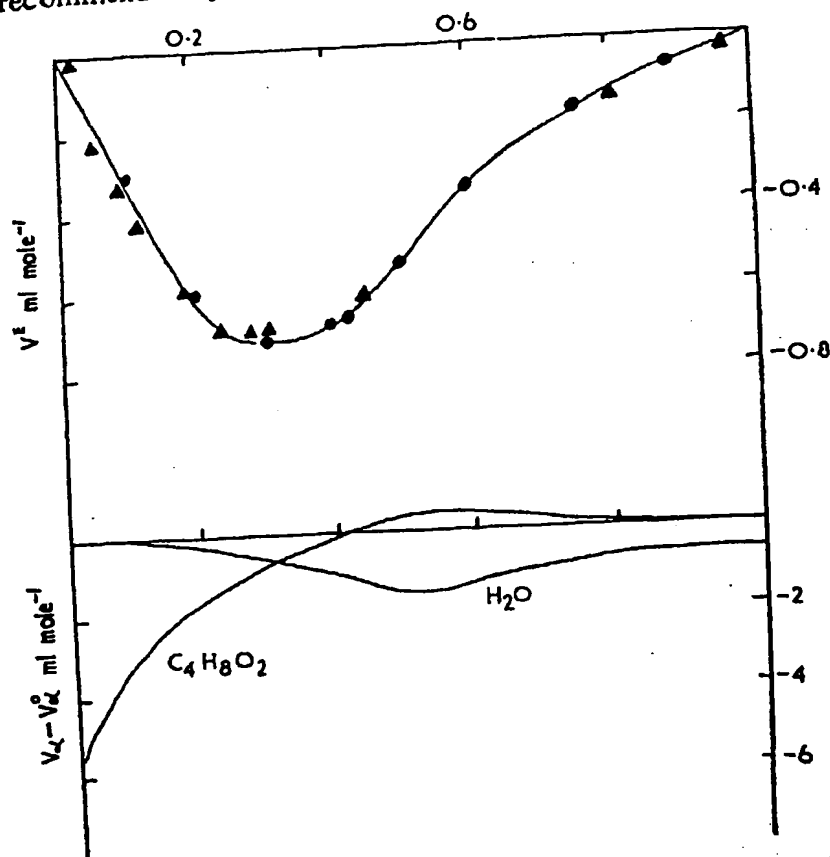


FIG. 10.—Excess volume at 25° C as a function of the mole fraction of dioxane, from Hovorka, Schaeffer and Dreisbach⁸ (circles), and from Griffiths (triangles). Partial molar volumes from the curve for V^E .

The heats of mixing were measured in a U-tube calorimeter which has been described previously.¹⁴

TABLE 4.—VAPOUR PRESSURES IN mm Hg

mole fraction dioxane temp. °C	0.000	0.260	0.535	0.760	0.820	1.000
100	760	1138	1151	1110	1077	733
110	1075	1571	1581	1496	1462	986
120	1489	2130	2135	2001	1953	1304
130	2026	2837	2833	2628	2556	1696
140	2711	3722	3703	3390	3265	2174
150	3571	4808	4763	4300	4181	2752
156	4184	5556	5517	4927	4785	3156

The vapour pressure of pure dioxane can be approximately represented by

$$\log_{10} p \text{ (mm Hg)} = 7.72713 - 1813.98/(t^\circ \text{C} + 273.16)$$

with a maximum relative error (at 100° C) of 0.4 %. The observed boiling point was 101.2° C. These results agree with the measurements of Højendahl¹⁵ within the error of ± 2 % which he assigns to his results.

TABLE 5.—HEATS OF MIXING AT 25° C

mole fraction dioxane	0.175	0.388	0.601
ΔH (cal mole ⁻¹)	-130.5	-30.4	+70.2

Three mixtures of mole fraction of dioxane of 0.18, 0.39 and 0.60 were heated in evacuated sealed tubes to 240° C in a bath of glycerol. Neither opalescence nor the separation of a second liquid phase was observed.

DISCUSSION

This system comes close to satisfying the conditions for a lower consolute point over the whole temperature range from 25 to 156° C. The excess free energy at 25° C is shown in fig. 8, and two estimates of that at 150° C in fig. 11. One of these estimates is based on the observed vapour pressures but with no correction for the deviations from the perfect gas laws. These deviations will be large but their relative effect on GE is probably not

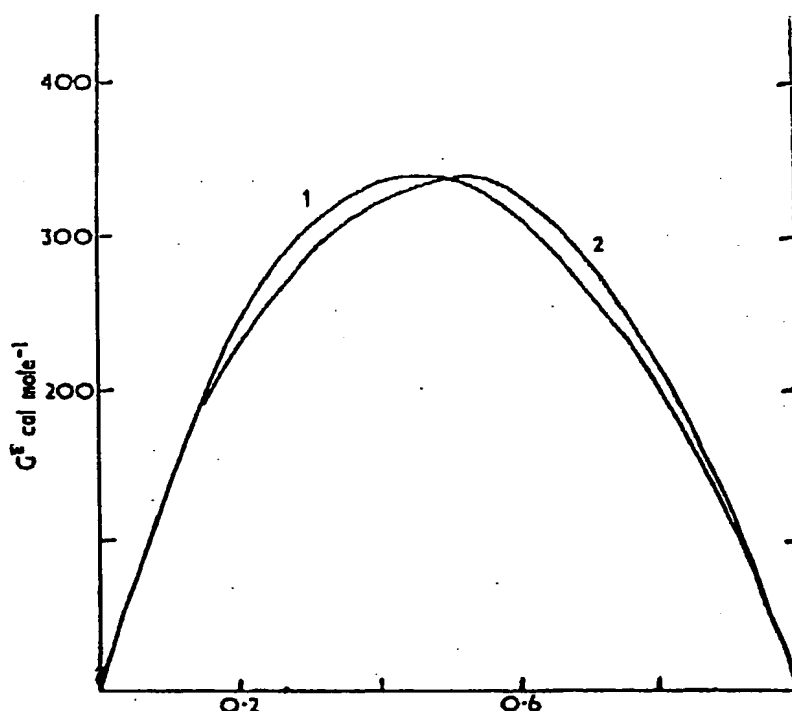


FIG. 11.—Estimates of GE at 150° C from (1) vapour pressures at 150° C and (2) from HE , SE and C_pE at lower temperatures (see text).

serious owing to its unusually large size. The second estimate is a calculation from HE and TSE at 25° C and C_pE at 40° C with the additional assumption that C_pE is independent of temperature. The agreement between the two estimates is remarkably good. It is found that GE is about 10 % too small for curves of these shapes, at both 25 and 150° C for the system to show a consolute point. This is in agreement with direct observation. The nearness of the system to phase separation is shown by the readiness with which this occurs in the presence of an electrolyte. For example, as little as 0.005 (mole fraction) of HCl causes phase separation at room temperature.¹⁶

A comparison of the properties of this system with solutions of polyethylene glycols is made in the body of this paper.

- ¹ Taylor and Rowlinson, *Trans. Faraday Soc.*, 1955, 51, 1183.
- ² Dorsey, *Properties of Ordinary Water Substance* (Reinhold, N.Y., 1940).
- ³ Beynon and Humphries, *Trans. Faraday Soc.*, 1955, 51, 1065.
- ⁴ Coffin, Devins, Dingle, Greenblatt, Ingrahim and Schrage, *Can. J. Res. B*, 1950, 28, 579.
- ⁵ Baughan, Jones and Stewart, *Proc. Roy. Soc. A*, 1954, 225, 478.
- ⁶ Geö, *Quart. Rev.*, 1947, 1, 282. Fricke and Lüke, *Z. Elektrochem.*, 1930, 36, 309.
- ⁷ Prigogine and Defay, *Chemical Thermodynamics* (Longmans, London, 1954), p. 431.
- ⁸ Hovorka, Schaeffer and Dreisbach, *J. Amer. Chem. Soc.*, 1936, 58, 2264.
- ⁹ Vierk, *Z. anorg. Chem.*, 1950, 261, 283.
- ¹⁰ Bacarella, Finch and Grunwald, *J. Physic. Chem.*, 1956, 60, 573.
- ¹¹ Stallard and Amis, *J. Amer. Chem. Soc.*, 1952, 74, 1781.
- ¹² Griffiths, *J. Chem. Soc.*, 1952, 1326; 1954, 860.
- ¹³ Morantz and Warhurst, *Trans. Faraday Soc.*, 1955, 51, 1375.
- ¹⁴ Thacker and Rowlinson, *Trans. Faraday Soc.*, 1954, 50, 1036.
- ¹⁵ Højendahl, *Danske Vid. Selsk. Mat.-Fys. Medd.*, 1946, 24, no. 2.
- ¹⁶ Robinson and Selkirk, *J. Chem. Soc.*, 1948, 1460.

Polypropylene Glycols (PPGs)

Overview

Polypropylene glycols are polymers of propylene oxide. They are clear, viscous liquids with low pour points. Viscosity increases and water solubility decreases with increasing molecular weight.

PPGs can be blended to obtain liquids with intermediate viscosities. The molecular weights range from low for water-soluble to high for water-insoluble applications.

Properties

Series	INCI/CTFA Nomenclature	Average Molecular Weight	Specific Gravity ⁽¹⁾	Average Viscosity ⁽²⁾			Flash Point ⁽³⁾	Average Pour Point ⁽⁴⁾	Cloud Point ⁽⁵⁾		Refractive Index ⁽⁷⁾
				25°C	40°C	100°C			1% aqueous	10% solvent ⁽⁶⁾	
Units			25/25°C	cSt	cSt	cSt	°C	°C	°C	°C	@25°C
P400E	PPG-12	425	1.007	68	31	5	>150	-49	>95	69	1.445
P600E	PPG-15	600	1.003	84	38	6	227	-47	65	57	1.4465
P1000E	PPG-17	1000	1.003	143	71	11	>150	-43	21	38	1.447
P1200E	PPG-20	1200	1.003	160	80	13	174	-41	20	32	1.448
P2000E	PPG-26	2000	1.002	230	143	24	198	-31	15	20	1.449
P4000E	PPG-34	4000	1.004	1110	438	73	185	-20	9	10	1.450

Test Methods:

¹ Specific Gravity: ASTM D 892

² Viscosity: ASTM D 445

³ Flash Point: ASTM D 92

⁴ Pour Point: ASTM D 97

⁵ Cloud Points: ASTM D 2024

⁶ 10% surfactant in a solution of 25% Diethylene glycol butyl ether in water.

⁷ Refractive Index: ASTM D 1218

Details

For additional information regarding any DOW products, please contact your local distributor.